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Atmospheric
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Discussions

Interactive comment on "Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: surface tension depression and secondary organic products" *by* Z. Li et al.

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Reviewer #1 Responses

We thank Reviewer 1 for his or her insightful and constructive comments. We address specific points below. (Reviewer comments in quotation marks, responses below)

"While the use of nearly saturated ammonium sulfate (AS) seems justified to simulate the environment of an aerosol particle, there should be some discussion of how the aldehyde concentrations (0.02 to 2 M) were chosen, how this compares to typical aldehyde concentrations in atmospheric aerosol, and whether any extrapolation between experimental and atmospheric conditions is necessary in order to assess the signifi-

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cance of the results."

We have added the following discussion to clarify this point within the manuscript, “Ambient aerosol concentrations of formaldehyde and acetaldehyde have been measured up to 0.26 μg m-3 formaldehyde and 0.4 μg m-3 acetaldehyde in Los Angeles (Grosjean, 1982). Using a specific aerosol volume of 10ˆ-10 m3 m-3 (Noziere et al., 2010), these ambient in-particle concentrations of formaldehyde and acetaldehyde correspond to 0.088M and 0.092M respectively, which are well within the concentration ranges used in this study. At these realistic ambient aerosol concentrations, we observed non-negligible surface tension depression by formaldehyde and acetaldehyde (7.1% and 9.5%, respectively). The extended concentration range used here was chosen to enable us to characterize the surface tension behavior using the Szyszkowski-Langmuir equation.”

"However, more explanation is needed as to why the same base compounds are often identified at different m/z in different runs, even though the same CIMS ionization conditions are used. For example, formic acid shows up at m/z 82 and 209 in Figure 5, but at 173 and 209 in Figure 6, where the organics are at higher concentration and MG is also present. Why should this affect the ionized form of formic acid detected?Similarly, formaldehyde acetal oligomers are identified in both Figure 5 and 6, but there are (surprisingly) almost no common m/z values. In this case, different formaldehyde acetal oligomers are identified, suggesting a complex influence of MG and concentration on acetal formation. If these issues could be addressed in the manuscript, it would only increase confidence in the product identifications."

We have added the following text to better explain this phenomena in the CIMS discussion, “While the negative-ion spectra of the formaldehyde-AS and formaldehyde-MG-AS mixtures share many similar peaks, there are some differences in the spectra. Small variations in pressure and flow rates within the declustering region can affect the clustering efficiency between the analyte and the parent ions, and surrounding water molecules, resulting in the same analyte compound appearing at different m/z values.”

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Regarding the formaldehyde hemiacetal oligomers, we will point out that when the H3O+ positive ion spectra (in the Supplementary Information) are also considered, we detect the n = 2,3,4,5,6,8,9 oligomers in the F-AS system, and the n = 2,3,4,5,6,8 oligomers in the F-MG-AS system. The differences seen in the F oligomer population can be attributed to some chains being consumed via cross-reaction with MG (e.g. cross-products containing 2 F and 1 MG were observed).

"Abstract line 13: The abstract should make clear what the changes in surface tension were for acetaldehyde and formaldehyde, rather than just listing the depressed surface tension values."

We have added the percent change in surface tension of acetaldehyde in both AS and H2O into the abstract. The text now reads, "Acetaldehyde depresses surface tension to 65($\pm$2) dyn cm-1 in pure water (a 10% surface tension reduction from that of pure water) and 62($\pm$1) dyn cm-1 in AS solutions (a 20.6% reduction from that of a 3.1 M AS solution)."

"Page 19480 line 18: The solution pHs are quoted as being near 3. Does this apply to the solutions in both AS and in water? If in water, what is the source of the acidity?"

We thank the reviewer for this point. We have clarified the text to read, "The pH value of the AS-containing reaction mixtures, measured using a digital pH meter (Accumet, Fisher Scientific), was 2.7-3.1. The acidity of the solutions is attributable to trace amounts of acidic impurities within the organic reagent stock solutions (i.e. pyruvic acid from the methylglyoxal stock solution)."

"Page 19482 line 15: Could the text state either the surface tension of pure water, or the percent reduction caused by acetaldehyde?"

The following text has been added to clarify, "The surface tension of acetaldehyde in water decreases rapidly and reaches a minimum value of 65$\pm$2 dyn cm-1 at 0.89 mol C/kg H2O (a 10% reduction from that of pure water, 72 dyn cm-1)."

"Page 19484 line 14: The earlier cited work on acetaldehyde-AS and acetaldehyde-H2O systems should be discussed in comparison to the products identified in this work. Were some of the same products observed in the earlier work as with the acetaldehyde-methylglyoxal (MG)-AS mixture in the present work?"

We have added the following statements to clarify the previous work within the CIMS discussion (section 3.2), “We did not perform Aerosol-CIMS analysis on acetaldehyde-AS or acetaldehyde-H2O solutions because these systems have been characterized extensively by others (Noziere et al., 2010; Casale et al., 2007). These studies showed the acid-catalyzed formation of aldol condensation products in solutions containing AS, and little reaction in the absence of AS..” and section 3.2.3, “The H3O+.(H2O)n spectrum for aqueous acetaldehyde-MG-AS mixtures is shown in Figure 7, with peak assignments listed in Table 4. Several peaks, specifically acetaldehyde aldol condensation products (i.e. 88.9, 107.2, 192.9, 289.6, and 297 amu), are similar to those expected in acetaldehyde-AS solutions (Noziere et al., 2010; Casale et al., 2007).”

"Page 19485 line 15: The manuscript notes that organosulfate species have not been observed before by proton-transfer MS methods. However, this statement may cause some to doubt that organosulfates were indeed detected in this study. Can the authors make an argument based on the literature that organosulfates should be expected to survive the analytical process – heating to 135 C to volatilize from aerosol particles? Alternatively, can an organosulfate standard be run to demonstrate that it is indeed possible?"

The reviewer is correct, organosulfates have never been detected by proton-transfer, or positive-mode, mass spectrometry. However, for this study, we detect organosulfates using negative-mode detection, using I- as the reagent ion. We have previously detected an organosulfate compound from methylglyoxal using the same instrument and experimental procedure (Sareen et al., 2010).

"Page 19486 line 1: Can the authors use their previously published MG-AS CIMS data

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to more conclusively identify the m/z 272 peak?"

Like all mass spectrometric techniques, Aerosol-CIMS cannot be used to differentiate between organic species of the same molecular weight within the instrument's mass resolution unless specific markers exist (i.e. a satellite isotope peak). Further post-analysis would be required to more conclusively identify the structure of the species at m/z 272.

"Page 19488 line 3: Presumably the solutions equilibrated with headspace in capped bottles, but this statement made me wonder about the nature of this equilibration. No details are given in the Methods section."

We have now clarified the text to read, “The reaction mixtures studied here equilibrated with the headspace of the closed container for 24 h before the surface tension measurements were performed.”

"Page 19488 line 11: This statement is almost certainly correct. However, it could be strengthened by including some references to atmospheric measurements."

We have changed the following text in the manuscript to read, “When formaldehyde and acetaldehyde are present in combination with MG, as would likely happen in the atmosphere (Fung and Wright, 1990; Grosjean, 1982; Munger et al., 1995) there is a synergistic effect. . .”

"Page 19489 line 1: Chemical name appears to be missing the term “sulfate.”"

Yes, thanks for pointing this out. We have updated the chemical name to include “sulfate."

"Page 19489 line 23: “Low solubility” seems like the wrong term here, since formaldehyde is highly soluble in water. The authors appear to be discussing the Henrys law coefficients and the transfer of aldehydes from the gas phase."

We have adjusted the text to read, “The relatively low Henry's Law partitioning of

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formaldehyde and acetaldehyde to water suggests that their potential to contribute to total SOA mass is low as compared to highly soluble species such as glyoxal."

"Page 19490 line 1: Is it possible to harmonize the cited results of Kroll et al. and Romakkaniemi et al.? If surface-active species enhanced SOA production, why wouldn't growth be observed in the experiments described in Kroll et al.?"

The simulations of Romakkaniemi et al. included OH oxidation of MG in the gas phase, whereas the experiments of Kroll et al. did not include photooxidation. Dark uptake of MG is much slower than that driven by OH chemistry in the aqueous phase, hence the enhancement effect predicted by the model of Romakkaniemi et al. was not detectable in the experiments of Kroll et al.

"Figure 2 c: It is not clear how formaldehyde can increase from 0 to 0.4 m while MG decreases from 1.5 to 0.4 m while the total organic concentration stays constant at 0.5 M in all experiments. Are there huge differences in solution density?"

The units for this figure (and all other figures describing surface tension) are mol carbon (kg water)-1. The difference in axes between formaldehyde and MG is merely the result of the large difference in mol carbon of the organics (1 mol C/mol formaldehyde and 3 mol C/mol MG), and is not related to the total organic concentration (0.5 M).

"Table S3 and S4: The C2H4O3 molecule is listed as appearing at m/z 95 in Table S3 but at m/z 96 in Table S4."

When taking the resolution of our CIMS into account, these peaks are identical. We have left the m/z where the peaks were identified for each graph unchanged in order to show the data more completely. However, to reduce confusion for the reader, we have added the following statement to the document in the CIMS discussion (section 3.2), "The CIMS data show products of self- and cross-reactions of formaldehyde, acetaldehyde and MG in pure water and 3.1 M AS. The resolution for all CIMS data presented here was m/z ±1.0 amu."

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"Page S6: equation S4 is unbalanced. The last paragraph mentions C2H6O5S on two occasions, when the correct formula is probably C2H6O6S."

Thanks for pointing this out. We have made the correction.

References:

Casale, M. T., Richman, A. R., Elrod, M. J., Garland, R. M., Beaver, M. R., and Tolbert, M. A.: Kinetics of acid-catalyzed aldol condensation reactions of aliphatic aldehydes, Atmospheric Environment, 41 (29), 6212-6224, 2007.

Fung, K. and Wright, B.: Measurement of Formaldehyde and Acetaldehyde using 2,4-dinitrophenylhydrazine-impregnated cartridges during the carbonaceous species methods comparison study, Aerosol Science and Technology, 12 (1), 44-48, 1990.

Grosjean, D.: Formaldehyde and other carbonyl in Los Angeles ambient air, Environmental Science & Technology, 16 (5), 254-262, 1982.

Munger, J. W., Jacob, D. J., Daube, B. C., Horowitz, L. W., Keene, W. C., and Heikes, B. G.: Formaldehyde, glyoxal, and methylglyoxal in air and cloudwater at a rural mountain site in central Virginia, Journal of Geophysical Research, 100 (D5), 9325-9333, 1995.

Noziere, B., Dziedzic, P., and Cordova, A.: Inorganic ammonium salts and carbonate salts are efficient catalysts for aldol condensation in atmospheric aerosols, Physical Chemistry Chemical Physics, 12 (15), 3864-3872, 2010.

Sareen, N., Schwier, A. N., Shapiro, E. L., Mitroo, D. M., and McNeill, V. F.: Secondary organic material formed by methylglyoxal in aqueous aerosol mimics, Atmos.Chem.Phys., 10, 997-1016, 2010.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 19477, 2011.